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THE DETERMINATION OF DETECTION LIMITS BY DC ARGON PLASMA ATOMIC--ETC(U)

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THE DETERMINATION OF DETECTION LIMITS BY DC ARGON
PLASMA ATOMIC EMISSION SPECTROMETRY

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INTRODUCTION

The application of any general analytical method for the determination of trace elements in solution depends on the detection limits obtainable, and the specificity, accuracy, precision and simplicity of the technique. The determination of detection limits under controlled experimental conditions is of considerable importance because the values obtained are a necessary guide to the analyst and provide a basis for comparisons with calculated minimum detectable concentrations.¹

This report summarizes detection limits measured for 19 elements, by DC Argon Plasma Atomic Emission Spectrometry (DCP), in the multielement mode. These results are compared to published detection limits obtained by Inductively Coupled Plasma (ICP) and Atomic Absorption (AA) methods.

EXPERIMENTAL

Standards. Solutions were prepared by standard methods² or purchased as high concentration standards for AA from Fisher Scientific Company and diluted appropriately. Multielement Standard Solutions were freshly prepared by mixing appropriate volumes and diluting the concentrated standards. For all solutions and blanks, water was better than ASTM Type I Reagent Water³, prepared from house distilled water polished by recirculation through a Milli-Q⁴ water purification system.

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Instrument. All emission measurements were made with a Spectrometrics SMI-III DC Argon Plasma Atomic Emission Spectrometer. The operating conditions employed in this study are as follows: Argon tank pressure, 80 psi; sleeve pressure, 50 psi; nebulizer pressure, 17 psi. Gas flow rate was 8 l/minute. Entrance slits were set at 50x300 microns and exit slits at 25x300 microns. For the multi-channel cassette operation, the active diagnostic PMT voltage varies; for the single channel cassette used for scanning, it was set at 800 V. Solution was nebulized at 3 ml/minute. In the multi-channel mode, each measurement is the result of three integrations of 10 seconds each. For scanned spectra, an X-Y recorder was used at 50 seconds/inch in the x direction and a Y sensitivity of 0.1 to 0.5 mv, depending on scale expansion desired.

The DCP discharge is generated when an arc is struck between the electrodes through which argon flows. Once ignited the plasma is sustained by low voltage. The Spectrospan III is equipped with a three electrode jet unit (two anodes and one cathode, Figure 1) and is capable of analyzing as many as 20 elements simultaneously. A control computer console performs integrations, switches signal sources from one PMT to the next, and calculates concentrations based on input standard values. The results are recorded on an interfaced printer.

Determination of Detection Limits. The method used here is similar to that described by Slavin⁵. Two concentrations are prepared with entirely separate glassware used for each to reduce the possibility of contamination to a minimum. The lower concentration is made approximately equal to the expected detection limit and the second standard is made twice this concentration. Inasmuch as routine multi-element analyses generally require multi-element standards for calibration, detection limits reported here are based on multi-element solutions. Therefore, for all these determinations, a low or high concentration standard also contains the remaining 18 elements at the same concentration as the element under study. After establishing optimum instrumental conditions, including maximum signal output at the focal plane of the Echelle prism spectrometer,⁶ proper slitwidth, plasma position and photomultiplier tube voltages, alternate measurements are

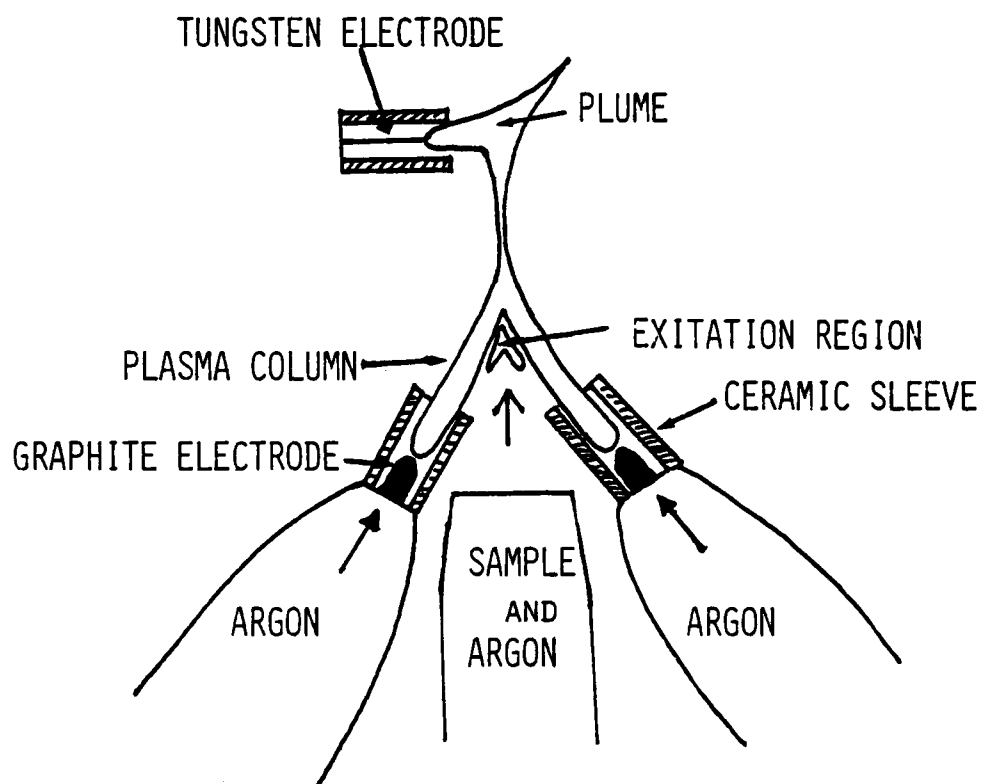


FIGURE 1 INVERTED Y CONFIGURATION OF PLASMA JET

taken of each standard until a total of sixteen readings of each have been made. A blank reading is obtained before each standard reading. The sequence is: blank, low concentration standard, blank, and high concentration standard. The concentration detection limit is calculated as follows:

$$\text{Detection Limit} = \frac{\text{Concentration of standard} \times 2\sigma}{\text{Mean}}$$

where σ is the standard deviation of the mean, and "mean" is the arithmetic mean of the 16 readings. Readings were normalized by subtraction of the average of the blanks before and after that standard. The calculation is made independantly for each standard high and low concentration and the final reported detection limit is the average of the two results. Assuming a normal distribution, the 2σ detection limit implies that a sample with concentration at this detection limit will result in a positive signal (greater than the arithmetic mean of the two blanks) 95% of the time.

Metal emission lines were scanned by friction coupling a synchronous motor to the monochromator wavelength selection wheel. During wavelength scans, the photomultiplier output was recorded, through a current to voltage converter, on an X-Y recorder (HP-7044A). Spectra were calibrated using several known emission lines in the region scanned.

RESULTS AND DISCUSSION

Table 1 lists the measured detection limits (95% confidence limits, or twice the standard deviation) for 19 elements together with the wavelengths of the analytical lines. Table 2 shows literature values for the corresponding detection limits obtained by Inductively Coupled Plasma (ICP) and Atomic Absorption (AA) methods⁷. It should be noted that the analytical wavelengths used for the three different techniques are not generally the same. The detection limits by DCP can be improved by using a single channel cassette and choosing appropriate analytical wavelength and slits. A comparison of relative detection limits observed by dcp using the multi-channel cassette, ICP and flame AA methods serve as a useful guide in the

TABLE 1 DETECTION LIMITS (MULTI-ELEMENT MODE) BY DCP

Element	Wavelength(nm)	Low Standard ($\mu\text{g/l}$) ^a	High Standard ($\mu\text{g/l}$) ^a	Mean Detection ($\mu\text{g/l}$) Limit
Li	610.3	2.5	3.5	3
B	249.7	9	11	10
Mg	279.5	1	2	1.5
Al	396.1	3	3	3
P	213.6	172	214	190
Ca	393.3	1	1	1
V	437.9	4	10	7
Cr	425.4	4	13	8
Mn	259.6	3	5	4
Fe	259.9	25	50	40
Co	345.3	5	12	9
Ni	341.4	5	9	7
Cu	324.7	1	3	2
Zn	213.8	9	15	12
Cd	214.4	10	18	14
Sn	317.5	285	307	300
Ba	455.4	0.5	1	0.8
Hg	253.7	134	150	140
Pb	283.3	32	44	40

a. Observed Values.

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TABLE 2 - COMPARISON OF DETECTION LIMITS ($\mu\text{g/l}$)

<u>ELEMENT</u>	<u>DCP</u>	<u>ICP*</u>			<u>AA*</u>
Li	3				
B	10	1	-	4	700
Mg	1.5	0.03	-	0.7	0.1
Al	3	0.4	-	2	20 - 30
P	190	4	-	33	53,000
Ca	1				
V	7	0.2	-	0.7	20
Cr	8	0.2	-	1	2 - 3
Mn	4	0.03	-	0.1	0.8 - 2
Fe	40	0.4	-	4	4 - 6
Co	9	0.3	-	2	2 - 7
Ni	7	1	-	2	2 - 5
Cu	2	0.2	-	0.4	1 - 2
Zn	12	0.2	-	2	1 - 5
Cd	14	0.1	-	1	1
Sn	300	9	-	25	1 - 150
Ba	0.8	0.09	-	0.5	8 - 50
Hg	140	6	-	30	360 - 500
Pb	40	1			10 - 11

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selection of the best technique. During the selection one should always consider the advantages and disadvantages of each method of analysis.

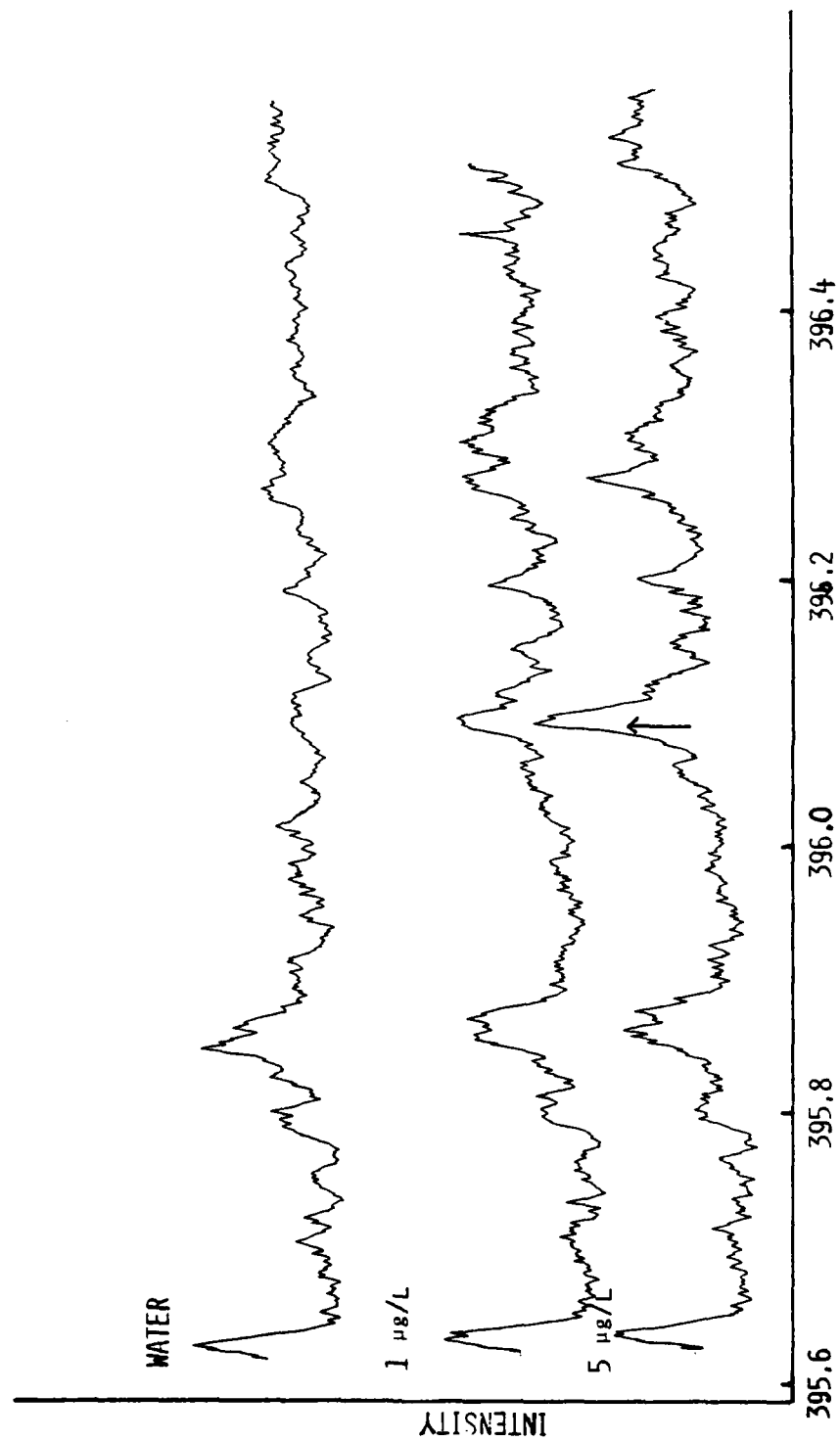
The selection of suitable analytical wavelengths for multi-element analysis is important. For example, in Table 2 a less intense 283.3 nm line was chosen for lead, instead of a more intense 405.8 nm line because we have found that boron enhances lead intensity at 405.8 nm.⁸

In general, the detection limits observed using the multi-channel cassette are found to be much higher than those obtained by the use of a single channel cassette. Figure 2 shows the wavelength scan obtained for 5 and 1 μg aluminum solutions and water using a single channel cassette. The signal output at the 396.1 nm line is examined.⁹ The signal-to-noise ratio for the 396.1 nm line shown in Figure 2 will allow a detection limit of approximately 1.0 $\mu\text{g}/\text{l}$ compared to the 3 $\mu\text{g}/\text{l}$ detection limit for aluminum using the multi-channel cassette.

The analytical sensitivity of the instrument tends to decrease with time because of the slight displacement of the region of the plasma where maximum emission intensity occurs. The displacement is caused by the continuous sputtering of the anode which is much faster when the electrode protrudes more than 4 mm from its sleeve¹⁰ and by slight but significant fluctuations of the optimum grating positioning which is probably due to vibration and temperature changes. Because of these factors, a standard must be read every 2 or 3 samples for reasonably good precision (relative standard deviation $\leq 5\%$). The movement of the region of maximum intensity of the plasma is impossible to control except by frequent readjustment.

CONCLUSION

It is important to note that detection limits, although carefully measured, are still rather nebulous quantities because the numbers obtained depend sensitively on the exact experimental conditions employed. The emission spectrometric detection of low concentrations of the elements is



WAVELENGTH (nm)
FIG. 2. EMISSION SPECTRUM FOR ALUMINUM

limited strictly by the signal to noise ratio. There is adequate documentation in the literature^{11,12} that the limiting factor is the ratio of the line signal to the statistical fluctuations and detector noise. Because the empirical detection limits reported here account for these statistical fluctuations they should provide more realistic values than those calculated on a less rigorous basis. Additional emission interferences such as that observed by boron in lead analyses⁸ are probably due to the higher temperatures used in plasma methods compared to AA and other methods. The possibility of additional interferences of this sort in plasma emission techniques requires empirical determination of detection limits under the conditions used for analyses. Such determinations are increasingly necessary to insure reliability of low level analysis results. This summary is intended to provide such a basis.

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